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ABSTRACT

These materials were designed to be used by life science students for instruction in the application of physical theory to ecosystem operation. Most modules contain computer programs which are built around a particular application of a physical process. This module describes the application of irreversible thermodynamics to biology. It begins with explanations of basic concepts such as energy, enthalpy, entropy, and thermodynamic processes and variables. The First Principle of Thermodynamics is reviewed and an extensive treatment of the Second Principle of Thermodynamics is used to demonstrate the basic differences between reversible and irreversible processes. A set of theoretical and philosophical questions is discussed. This last section uses irreversible thermodynamics in exploring a scientific definition of life, as well as for the study of evolution and the origin of life. The reader is assumed to be familiar with elementary classical thermodynamics and differential calculus. Examples and problems throughout the module illustrate applications to the biosciences. (Author/CS)

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THERMODYNAMICS OF IRREVERSIBLE PROCESSES

by

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and

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PREFACE

Thermodynamics of irreversible processes is discussed in this module in a broad perspective of major biological applications. The reader is assumed to be familiar with elementary classical thermodynamics and to have some exposure to differential calculus. Biological examples and problems are used throughout this module to facilitate understanding.

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INTRODUCTION

Thermodynamics provides a powerful tool for describing the characteristics of biological systems because life processes involve the transformation of energy and matter. Thermodynamic principles underlie such processes as convection, the conduction of heat, diffusion, radiation, absorption, respiration, transportation and photosynthesis. These, and other processes, may be limiting or controlling in such ecological phenomena as organism adaptation, ecosystem productivity, forest succession, animal foraging, species diversity and climate-ecosystem interactions. (For a review of the principles of thermodynamics in the context of ecology, see Gallucci, 1973.) A thermodynamics-based approach has also been used to investigate the processes of growth and development, as well as the origin of life and evolution. And perhaps most importantly, thermodynamics has been useful in discussions of a central problem, the stumbling stone of biology, namely, "What is life?" That is, what is the distinction, if any, between a living organism and a nonliving object?

This module describes the basic relationships of irreversible thermodynamics as applied to biology. We start by defining several basic notions such as the concepts of a system and a system's states, thermodynamic processes and variables, including energy, enthalpy and entropy. Next, we review the First Principle of Thermodynamics which is always a starting point for any introduction to thermodynamics. The Second Principle of Thermodynamics is treated extensively to demonstrate the basic differences between reversible and irreversible processes. The notion of entropy is shown here to play a central role the the discussion. This is followed by a proof of the main theorem of modern thermodynamics (Prigogine's theorem) demonstrated by two simple examples. This proof may be skipped

without any loss in continuity. Finally, a set of theoretical and philosophical questions, pertaining to the core of biological thermodynamics, is discussed. This last section includes the use of irreversible thermodynamics toward a scientific definition of life, as well as for the study of evolution and the origin of life.

A companion module entitled "Irreversible Thermodynamics for Ecosystems" has further applications of thermodynamic principles to biology and shows by ecological examples how the principles actually can be useful in practical research. Although the present and the companion modules are self-contained, a student would find it advantageous to be familiar with elementary thermodynamics (see, e.g., Waser, Trueblood, and Knobler, 1977 or Stevenson, 1979a,b).

BASIC TERMINOLOGY WITH EXAMPLES

Before we start our discussion about the concepts of modern thermodynamics and its applicability to biology, a certain terminology and notation should be introduced. First, we define and classify systems, states and processes.

A system may be defined as a bounded complex of interacting elements. This is a very general definition; it can be applied to virtually everything which consists of smaller parts. Examples are an atom, a molecule, a cell, an organ, an animal, a man, a society, a country, an ecological community, the whole biosphere, the solar system, or even the universe. Two main characteristics of systems must be stressed: (1) the elements are interacting; (2) a system is enclosed by a (often imaginary) boundary. For example, an ecosystem (say, an ecological community) is a complex of

interacting organisms enclosed within a limited environment. Each system consists of subsystems and they, in turn, consist of even smaller systems and so on. This is often described as a hierarchy of a system's elements.

A system is called open if both energy and matter are exchanged across its boundary with the surroundings; a system is closed if there is only an exchange of energy; and a system is isolated if neither matter nor energy is exchanged. A closed or isolated system is said to be in equilibrium state if no macroscopically measurable changes occur or if its physical properties do not change in time. Generally speaking, mechanical, thermal, chemical or electrical gradients (differences in potential energy) will act to cause flows of mass and/or energy which act to decrease the differences. However, given enough time, the gradients in a closed or isolated system vanish, resulting in the equilibrium state. Molecular fluctuations, of course, continue to exist, but no macroscopic change is occurring.

Open systems may be in a remarkable condition called a steady state, which is not equilibrium since flows (gradients) of matter and energy can be sustained. In a steady state, however, the flows occur at a constant rate $\left(\frac{d}{dt}\ (\text{flow}) = 0\right)$ so that the input and the output of the energy and/or matter are balanced and the amount of energy and matter in the system is kept constant. Thus, a closed system or open system may be viewed as being enclosed by a boundary with an input (source) and output (sink) attached. Suppose the time rate of input of mass and/or energy is constant. The open system will eventually transmit energy and/or matter to the output, and if the rate of output is also constant, the system will, after some time for adjustment, achieve a steady state. Furthermore, it is entirely possible for a system to utilize the input energy to do work and to realize the

energy in an alternative form. For example, an animal gets its energy through food consumption which enables it to move (work) and keep its body at a constant temperature (energy realization in the form of heat).

Open systems that have reached a steady state or are approaching it are characterized by a number of remarkable properties (von Bertalanffy, 1968). One of these is the so-called equifinality, namely the fact that a steady state is independent of the initial conditions and is determined exclusively by the rates of reactions and the flows. The phenomena of overshoot and false start may occur in open systems approaching a steady state when a system has either gone beyond the steady state or initially evolved in a wrong direction. Eventually, both overshoot or false start lead to a steady state.

These features, common to all open systems, be it a cell, an organism or an ecological community, imply some sort of regulation and organization. However, organisms (open systems) differ from mechanisms (closed systems) in this respect. Following von Bertalanffy, we distinguish between the dynamic interaction of elements in open living systems and a simple feedback (regulatory mechanical) system as discussed in cybernetics. Feedback systems are usually open only to information but are closed to energy and matter. In most living organisms, however, feedback systems are responsible for secondary regulations; thus dynamic open systems which can be primary regulators are of great interest.

Energy and/or matter flows within a system and through its boundaries are generally called processes. A process is termed reversible if it can be reversed in time, by expending the same amount of energy as was consumed by the original process moving in the original direction. This definition is most aptly thought about in the context of situations

where some gradients exist. To be reversible, the process must be able to go against these gradients. In other words, suppose a process initially is going in the direction of decreasing gradients when, at some point, it reverses and goes backward until it reaches the starting point. Although no real process is truly reversible, this idealization often serves as a useful approximation of some real processes. For example, the compression of a gas by a frictionless piston in the cylinder of a car engine may be considered a reversible process. Classical thermodynamics is based upon the fact that reversible processes are sometimes very good models of real processes. Nevertheless, the use of such approximations for real, especially living, systems which function because of the presence of many, often coupled, irreversible changes is not generally appropriate. Therefore, biologists must appeal to a modern branch of thermodynamics, namely, the thermodynamics of irreversible processes (often called irreversible thermodynamics). By irreversible process, we mean a process that goes spontaneously in the direction of decreasing gradients and cannot be completely reversed. The important conceptual difference between the two kinds of processes will be further clarified in a later section which discusses the Second Principle of Thermodynamics.

All processes can also be divided into those which are <u>linear</u> and <u>nonlinear</u>. The formulation of laws that describe linear processes contains coefficients that premultiply the variables of interest (dependent variables) and are constants with respect to independent variables (such as time). Take the model of exponential growth, for example:

$$Q(t) = Q_o e^{at} \quad .$$

In ecology, this law may describe the unlimited growth of a population[1], with Q_o the number of organisms at time t=0, Q(t) the number of organisms at time t, and a constant "a" which is greater than zero if the birth rate is higher than the death rate. However, if "a" is a function of time, that is, a=a(t), the process is nonlinear. Intrinsic nonlinearities may arise in chemical and biochemical systems through auto- and cross-catalysis, inhibition, activation, template synthesis, etc.

In many applications of thermodynamics, transport processes are used to represent the flow of heat and mass between the environment and the system and within the system. Such processes are frequently denoted as phenomenological, or empirical and are usually approximated by linear relationships. The linear equations describing many transport processes are not derived from "the first principles" (e.g., the Principles of Thermodynamics) but instead result from fitting linear models to observed data. Examples of transport processes in ecology that can be approximated as linear are convection, conduction radiation, absorption, diffusion and transpiration. Linear approximations, although not always reasonable, are nevertheless desirable since they are easy to treat mathematically. Thus far, thermodynamics has dealt almost exclusively with linear models. In fact, the triumph of classical thermodynamics in physical chemistry was possible because the reactions could be considered to have constant rates and, consequently, as linear. Moreover, in many cases, the chemical reactions of inorganic chemistry are quite reasonably reversible, and therefore classical thermodynamics was applicable and appropriate.

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[1]Of course, this is only a model and therefore is limited in representing reality. Since no populations become infinite in size, this model is useful only for some bounded time intervals.

Thermodynamics, which is designed to deal with open systems and irreversible processes, that is, with situations typical of living organisms, is also based on the assumption of linearity of the processes. However, many important biological processes (such as biochemical reactions) often exhibit intrinsic nonlinearities. This may be the reason why, successful as it has been in other fields, irreversible thermodynamics has not yet fulfilled the expectation of becoming a unified basis for biology in the same way as classical thermodynaimcs has for chemistry.

Stability and fluctuations. It is important to distinguish between the steady states close to and far from equilibrium. The distance from thermodynamic equilibrium is expressed in terms of a certain measure of how the thermodynamic state variables differ from the values they have at the state of equilibrium. A mathematical expression for this measure is given in a later section on Prigogine's theorem.

An open system may have a steady state in the neighborhood of thermodynamic equilibrium. Such a state is always stable with respect to arbitrary fluctuations. That means that small fluctuations about this steady state tend to vanish and the system eventually returns to the initial (unperturbed) steady state. On the other hand, an open nonlinear system may reach a steady state that is far from equilibrium. For time independent boundary conditions (constant inflow and outlfow of energy and matter), such states may exhibit an equilibrium-type behavior. The set of such steady states is called a "thermodynamic branch" (Glansdorff and Prigogine, 1974). However, owing to possible nonlinearity and nonequilibrium boundary conditions, all of the steady states in this branch are not necessarily stable. In fact, under certain conditions, depending on the nature of the system, small initial fluctuations from the steady state may actually

become amplified and eventually lead the system to a new steady state associated with a changed spatial distribution of the system's elements. In other words, far from equilibrium, microscopic fluctuations may cause instabilities and lead to macroscopic changes in a system's parameters--occasionally, it is thought, in the direction of increased orderliness and away from equilibrium. This process has been proposed as a basis for the explanation of the phenomenon of pre-biological evolution (Glansdorff, 1977) as well as for certain peculiarities of energy metabolism during some stages of embryogenesis and development. The process has been referred to as "order through fluctuations" (Prigogine, Nicolis, and Babloyantz, 1972).

In addition to providing a possible scientific framework for viewing evolution and ontogenetic arguments, it was suggested that less grandiose phenomena may also be explained by this process. The depolarization of the membrane of a nerve cell, e.g., can be interpreted as a reaction of a charged cellular system being driven far from equilibrium by the difference in charge density on the two sides of the membrane; another example is viewing the formation of colonies of unicellular organisms as an instability of the uniform distribution of individual cells.

These introductory remarks are intended to present a broad context in which to view the applications of thermodynamics to objects that most closely resemble biological (viz. ecological) systems. However, the formalism of open system thermodynamics must first be discussed in more detail.

The transition of the open nonlinear system between unstable steady states on a thermodynamic branch is associated with a high degree of energy dissipation. The resulting orderliness is called a <u>dissipative structure</u>,

which is a generic name given to the ordered structures created in open systems found far from equilibrium as a consequence of a great amount of energy dissipation. For example, organic oxidation and other biochemical reactions that create dissipative structures have been produced in laboratory conditions. Consider a phenomenon of thermal convection in a fluid, for example. A small temperature gradient results in the redistribution of thermal energy and in random fluctuations of molecular energies. When a temperature gradient is increased beyond a critical value (a critical distance from equilibrium), instability causes the creation of macroscopic convection patterns ("structures"). This created orderliness appears to depend to a certain extent on the form of the initial perturbation; that is, the open system "remembers" the past events. Other types of conditions may lead to ordered structures that are periodic in time (a basis for a "biological clock"). Oscillations of variables (such as chemical concentrations) occur and may lead to characteristic temporal patterns (the reaction of glycolysis, for example, is oscillatory with specific periods and amplitudes).

We now proceed with the definitions of basic thermodynamic variables that are essential for further discussion. Some of the terms, like temperature, pressure or energy, are already familiar to the reader from other modules or courses. To begin with, recall how temperature and pressure are defined and measured. By <u>temperature</u> (θ), we mean a physical quantity that measures the degree to which a particular body is heated. It is also a measure of the average kinetic energy of the molecules of a system. This definition, however, is not precise for very low temperatures where energy is not a linear function of the temperature; however, the definition is acceptable in the temperature range of living matter which is the range

of most interest. In thermodynamics, temperature is conventionally measured on the absolute (Kelvin) scale. The conversion formula from degrees Celsius to degrees Kelvin is

$$\theta(K) = \theta(^{\circ}C) + 273.15 \quad . \tag{1a}$$

Another variable that plays an important role in thermodynamics is pressure (p). It represents the differential of force (F) acting normally on a corresponding differential area (A):

$$p = \frac{dF}{dA} \quad . \tag{1b}$$

Pressure may be measured in bars:

$$1 \text{ bar} = 10^5 \text{ Nm}^{-2} \text{ (SI)}$$

with dimensions $ML^{-1}T^{-2}$, where SI stands for the "Systeme International" units. Both pressure and temperature represent certain aspects of molecular motion and therefore are critical for describing any process involving heat and mass transfer.

An even more important thermodynamic variable is energy, a scalar measure of the various forms of motion. Alternatively, we may say that energy is a measure of a system's ability to produce work. Everyone is familiar with such forms of energy as thermal (heat), mechanical (movement), chemical, electric, radiation, gravitation, etc. Every form of energy may be described as either kinetic (movement) or potential (interaction of parts). Thus, mechanical energy evidently can be kinetic, while gravitation is potential. Potential energy may be transformed into kinetic (as is the case with a falling body) and vice versa. Moreover, generally speaking, any form of energy may be transformed into any other form--with a co-production of heat.

This phenomenon plays a crucial role in thermodynamics and will be discussed in detail in subsequent sections. Since heat is a co-product of any transformation of energy, it is important to understand its nature. Heat (Q), or thermal energy, represents the molecular motion in a system. It contributes to the total internal energy (U) which is a term coined to describe a function of state of a system that is usually composed of a sum of the kinetic and potential energy of its parts. By "function of state," we mean any quantity that under certain conditions can be expressed in terms of directly measurable variables, such as pressure, temperature, etc.

Another important form of energy is work (W). It is a mechanical form of energy formally expressed as $W=F\times L$ where F is a (constant) force and L is a displacement caused by this force. One should avoid an erroneous impression that work is something indistinguishable from action or, say, behavior, as is implied in colloquial usage. The term is employed in science to represent any mechanical energy that is used by a system to maintain a certain state (for example, the work done by the heat, or by muscles, or even by intestines digesting food). All organisms use energy to produce work and much of their work is needed to maintain the state of living. Table I gives a list of daily energy requirements of various types of organisms. The comparison shows that man needs less energy per body weight to maintain life than other species. This probably reflects a high efficiency of energy transformations in Homo sapiens.

Table I. Daily energy requirements in Kcal g^{-1} live body weight (from Odum, 1971.

Man	0.04
Small bird or mammal	1.0
Insect	0.5

Both energy and work are measured in joules (SI) or calories with dimensions $[ML^2T^{-2}]$. The module on units and dimensions (Fletcher, 1977) contains a full discussion of changes of units. It might be well to conclude the discussion of energy by a partial list of energy transformations in organisms (Table II). Chemical energy or such molecules as ATP is released in the form of work in muscles while other chemical interactions are responsible for secretion and active transport of ions through the membranes which are, in turn, connected with electrical discharges in nerves. Chemical transformations taking place in the processes of assimilation and synthesis correspond to redistribution of chemical energy by disintegration of some molecules and forming new bonds, etc. Radial energy (light) activates electrical processes in eyes or helps the formation of organic compounds in chloroplasts. Of course, this list is far from being complete.

Table II. Energy transformations in organisms.

Chemical	-	mechanical (work) muscles, heart, flagellar motion, etc.
Chemical	-	mechanical (osmosis) secretion, digestion, "ion pumps," etc.
Chemical	-	electric impulse in nerves, electric organs in some fishes
Chemical	-	chemical assimilation, synthesis
Chemical	-	light glow-worms, fireflies, luminoforous bacteria
Light	-	electric retina
Light	-	chemical CO_2 assimilation by plants
Magnetic	-	electric iron-sensitive bacteria in bird eyes
Mechanical	-	mechanical energy storage in bird feathers and the tendons of running birds and mammals

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Can you think of more examples?

One might logically ask how energy is exchanged between a system and its surroundings or between different subsystems. It turns out that, although energy is conserved in transfromations, no exchange is really one-to-one. This point will be clarified in a subsequent section dealing with the Second Principle of Thermodynamics. It is emphasized, however, that any energy transformation is accompanied by a corresponding quantitative change in a certain variable called <u>entropy</u>. Entropy (S) is a function of state also. It is used to express a "quality" or "rank" or the different forms of energy, or, to use other words, to quantify energy transformations. Physically, entropy is associated with the energy needed in order to return the system into its initial state after some energy transformation occurred. A derivative of entropy with respect to time is called <u>entropy production</u> (P), that is, $P=dS/dt$. It will be seen that for equilibrium, $P=0$, while for nonequilibrium states, $P>0$.

In classical thermodynamics, it was found that in a closed system the ratio of the heat lost or gained (during a reversible process at a constant temperature) to the magnitude of this temperature (in K) is equal to the change in entropy, that is

$$dS = \frac{dQ}{\theta} \quad \text{or} \quad \theta dS = dW \ . \tag{2}$$

By the First Principle of Thermodynamics, the heat gained by a system is equal to the change in internal energy (U) plus the work (W) done by the system on its environment (it is known in physics, that for a gas under constant pressure, $dW=p\cdot dV$, where V is the system's volume), i.e., $dQ=dU+pdV$. Thus, in terms of the system's parameters

$$\theta dS = dU + dW = dU = pdV \quad . \tag{3}$$

In modern applications, it has been postulated also that entropy estimates the likelihood that a certain energy transformation takes place. As we will see later, energy forms corresponding to less entropy content are more likely to convert into those that have more entropy. Entropy is measured in the so-called entropy units (e.u.), that is, in calories per degree Celsius, or else in joules per degree of temperature. The entropy dimensions are $[L^2MT^{-2}\theta^{-1}]$.

In (2), the expression for all heat dQ can be subdivided into the heat due to exchange, dQ, and the heat that characterizes irreversibility of the system (the so-called non-compensated heat), dQ. Equation (2) becomes

$$dS = \frac{dQ_1}{\theta} + \frac{dQ_2}{\theta} \quad .$$

Equations (2), (3) and (4) are different forms of a law initially discovered by Sadi Carnot in 1824 and later modified by R. Clausius. The Carnot-Clausius equations represent the degradation of energy. For open systems involving mass transfer, the Carnot-Clausius formula has an additional term due to entropy supplied through mass exchange such as diffusion and convection:

$$dS = \frac{Q_1}{\theta} + \frac{Q_2}{\theta} + s_i m_i \tag{5}$$

where m_i is the mass added to the system and s_i is its entropy for i^{th} component per unit mass. Thus, the additional term in (5) reflects the entropy change owing to the mass transfer through the system's boundary (see Tunell, 1977).

Each form of energy has its own characteristic entropy. A larger entropy is associated with a lower "quality" of energy (energy of "lower rank"). A low-quality energy differs from a high-quality energy of equal

joules in that the high-quality energy can be converted into useful work more efficiently than low-quality energy.

Table III gives the entropy content of some common forms of energy. It was found experimentally that entropy varies approximately inversely with the temperature associated with a particular form of energy. Use of this relationship makes it possible to calculate the entries in Table III. Note for example that gravitation has no associated temperature, so its entropy is zero but cosmic microwaves are "warm" and have the largest content of entropy per unit energy. Energy and entropy generally flow from upper to lower levels in the table, as will be shown in a later section of the present module. An interesting and yet unexplained phenomenon is that, in the universe, the energy of gravitation which is highest in rank is also predominant in quantity, although all forms of energy tend to be converted into microwaves which represent an ultimate heat sink.

Table III. Forms of energy and their corresponding entropies per unit energy expressed in units of inverse electron volts (from Dyson, 1971).

Gravitation	up to 10^{-10}
Nuclear reactions	10^{-6}
Internal heat of stars	10^{-3}
Sunlight	1
Chemical reactions	1 - 10
Terrestrial waste heat	10 - 100
Cosmic microwave radiation	10^{4}

As emphasized earlier, heat and work are the two important forms of energy that are usually produced when energy is exchanged. Suppose that heat at temperature θ is used to produce work. The result is that the temperature is reduced to θ_2. The maximal fraction of heat free to do work is proportional to $\frac{\theta_1-\theta_2}{\theta_2}$. Therefore at higher temperatures, heat has higher rank. A common measure of heat or work pertaining to a system is provided by a variable named <u>enthalpy</u>. Enthalpy (H) is a function of state defined by

$$dH = dU + d(pV) \tag{6}$$

where V is the volume of the system. By taking the differential of pV as a product term, it follows that for constant p, $dH = \theta dS + pdV$, while for constant p and V, $dH = dU$. Thus, dH represents the heat that is gained or lost by the system through the boundary in the process of energy exchange with the ambient media, under the conditions of constant pressure and volume. For example, in physical applications, enthalpy is widely used in chemistry and engineering as a measure of work needed to perform a task such as the compression of a gas.

A common way of measuring the enthalpy of biological materials is to measure the heat of combustion ("caloric value") at constant θ and p. This is done by the use of a bomb calorimeter. Table IV gives the caloric values of the three main groups of biological substances. It is seen that fats are almost twice as rich in energy as other compounds, illustrating the fact that fats are generally used for energy storage in animals. In contrast, starches and glycogen store the energy in plants.

Table IV. Average enthalpy content (caloric value) or organic materials in calories per gram (from Odum, 1971).

Fats	9.1
Carbohydrates	4.8
Proteins	4.8

Table V below provides a basis for comparison of the caloric values of the different kinds of organisms and also relates the energy levels between different parts of plants. The caloric value of a living organism depends on species, nutrition, age and many individual factors. However, some generalizations are possible. Caloric values of animal tissues are more or less constant. Except under starvation or storage conditions, animal tissue has about 5000 cal/g dry wt. Caloric values of plants are more dependent on seasonal activity and therefore assume values over a larger range.

Table V. The estimated enthalpy content (caloric value) per one gram of dry weight of biological material in kcal (compiled from Odum, 1971, and Golley, 1961).

Terrestrial plants	
Leaves	4.2
Stems and branches	4.3
Roots	4.7
Litter	4.2
Seeds	5.1
Overall	4.5
Algae	4.9
Molluscs	4.6

Table V (cont.)

Invertebrates (including insects)	3.0
Insects only	5.4
Earthworms	4.6
Vertebrates	
Mice	5.2

In ecological applications, it is often convenient (Wiegert, 1968) to express the net change in the enthalpy of a living system (organism) during some time interval Δt as

$$\Delta H = -\Delta H_m - \Delta Q - \Delta W \qquad (7)$$

where $\Delta H_m \equiv$ net change in enthalpy of the matter that entered and left the system, corresponds to the enthalpy content of ingested matter (I) minus that of egested and excreted matter (E); $-\Delta Q \equiv$ difference between the total amount of heat passing into and out of the system, equal to heal loss due to respiration (R) plus the heat loss owing to a direct heat exchange with ambient media. The latter term, however, tends to zero in the long run because the temperature of a homeothermic organism is usually approximately constant; $-\Delta W \equiv$ the network exchange which is usually much smaller than the internal work used to maintain the state of life and ultimately is dissipated as heat. Therefore, ΔW is generally omitted from most energy budgets. Consequently, we may rewrite (7) in the form

$$H = I - E - R \ . \qquad (8)$$

Negative signs in (7) reflect the fact that positive net enthalpy of matter,

as well as heat and work, cause a net loss from the system. The loss of metabolic heat (R) is usually measured indirectly through O_2 consumption.

To calculate the change in enthalpy in a specific food chain, one might suggest that

$$\Delta H = H_p - H_c$$

where H_p and H_c are enthalpy content of producer and consumer, respectively, per unit biomass. This approach might also be used to estimate the rate of energy transport along different paths of a food web but it would be strictly valid only if producer and consumer (say, the grass and a cow) differ by energy level and not by chemical structure. Ecologists interested in energetics still seek a way to account for evident structural differences between interacting organisms.

Finally, another variable that often plays an important role in thermodynamical considerations is <u>free energy</u>. It is a function of state that represents the internal energy of a system if certain conditions are fulfilled. Thus, <u>Gibbs free energy</u> (G) is defined under the conditions of constant temperature θ and pressure p by

$$G = H - \theta S = U + pV - \theta S \qquad (9)$$

or, in differential form,

$$dG = dH - \theta dS \quad . \qquad (9a)$$

The Gibbs free energy is the maximum amount of work a system can produce at constant θ and p. In isolated systems, there is no energy exchange ($dH=0$) and $dG=\theta dS$, so that for constant θ, the decrease in free energy corresponds to the increase in entropy. Gibbs free energy is a very

important function for biological applications since many life phenomena take place at constant atmospheric pressure and constant ambient temperature (or approximately constant θ owing to homeostasis). Note that free energy has the highest rank because it is convertible entirely into useful work. The present convention is to assign ΔG as a negative quantity for endothermic reactions (to represent reactions that absorb heat).[2]

Example: Under the standard conditions (25°C and 1 atm. pressure), the photosynthetic reaction

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 = 6O_2$$

is accompanied by the following changes in thermodynamic variables:

$\Delta G = -686.5$ kcal

$\Delta H = -669.9$ kcal

$\Delta S = -57$ e.u.

$\Delta U = 673.1$ kcal .

Examples showing how these and other thermodynamic quantities may be obtained are discussed in a companion module entitled "Irreversible Thermodynamics for Ecosystems."

Exercises and Review Questions

1. Consider various examples of systems with respect to a statement:

   "A system is not equal to the sum total of its parts."

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[2]Many chemical tables use this sign convention for free energy, entropy and the heat of reaction. It should be emphasized, however, that in engineering texts, the convention is the opposite: sign is taken as negative when heat is evolved. The exact meaning of the algebraic signs must therefore be understood before the data are used.

2. Consider a living system in a steady state, say, a mouse. Can it achieve an equilibrium state? What is the state called in common language?
3. In what sense is the cell, as a living system, open?
4. Consider a plant and an animal system. What are their hierarchical levels? In other words, what subsystems can you identify within a plant or an animal?
5. Consider a pond as a system. What are the elements of this system? Consider the littoral zone as a system; what are its elements? Consider a molecule of water from the pond; what are its elements? Practically speaking, is this system (the pond) open, closed or isolated?
6. Consider the earth as a system. Practically speaking, is it open, closed or isolated?

THE FIRST PRINCIPLE

The First Principle of Thermodynamics was discussed in previous modules under the name "The First Law." Many authors including the founding fathers of thermodynamics Sadi Carnot, R. Clausius and Lord Kelvis (see Magie, 1899) prefer to call this "law" a "principle" simply because it has a more general meaning than a scientific law: an empirical phenomenological law always has a limited scope of applications, the limits being determined by initial conditions, range of temperature, pressure, velocity, etc. For example, Newton's laws are not applicable for very large velocities; in ecology, laws of population growth depend on many parameters that in turn depend on temperature, specific interspecies interactions, etc. On the other hand, a principle has a more universal meaning and is supposed to be

applicable to the whole universe. An empirical or phenomenological law is usually inferred from observations while a principle is deduced from general reasoning. In fact, we are discussing a well-supported hypothesis that is universally accepted because of lack of contradicting evidence. In fact, the First Principle of Thermodynamics is simply a reformulation of the universal law of conservation of energy which is true subject to provisions for energy-mass transformations. In thermodynamic terms, this principle may be stated as

$$dU = 0 \text{ for isolated systems} \tag{10a}$$

$$dU = dU_{in} - dU_{out} \quad \begin{cases} \text{for closed and} \\ \text{open systems} \end{cases} \tag{10b}$$

where U is the net change in internal energy, dU_{in} and dU_{out} are the amounts of energy (for closed systems), or energy and mass (for open systems), flowing respectively, in and out across a system's boundary in some short time dt. There are many alternative formulations of this principle, the most common being

$$\Delta U = \Delta Q - \Delta W \tag{11}$$

where ΔQ is the net heat exchange with the surroundings and ΔW is the net work exchange with surroundings. ΔU is actually the difference between the energy level of the system in the final state, U_2, and that in the initial state, U_1. However, both U_1 and U_2 are hard to estimate because they involve the energy associated with nuclear forces, chemical bonds, kinetic and potential energy of molecules, etc. But ΔU can be measured directly if the form of the energy transfer is known. In differential form, (10) is

$$dU = dQ - dW = \theta dS - pdV \quad . \tag{12}$$

In general, when work other than mechanical is involved, (12) should be modified correspondingly. In case of chemical reactions, for example, we have to introduce the so-called chemical potential (μ_i) of the i^{th} component of the reacting system (i=1, 2, ... , k), which relates chemical work to the number of moles transported. It was determined empirically that

$$\mu_i = R\theta \ln c_i \tag{13}$$

where R is the universal gas constant and c_i is the concentration of the i^{th} component. If dn_i is the differential change in the mass of the i^{th} component, then the work of the mass transport due to the chemical reaction is

$$W_{chem} = \sum_{i=1}^{k} \mu_i n_i \tag{14}$$

where k is the number of components. Equation (12) takes the form

$$dU = \theta dS - pdV + \sum_i \mu_i n_i \quad . \tag{15}$$

The First Principle in this form is called the equation of Gibbs. For future reference, we may note that under the conditions of equilibrium (dV=dU=0) and (15) takes a particularly simple form

$$dS = \frac{1}{\theta} \sum_i \mu_i n_i \tag{16}$$

Exercises

1. The energy balance in an ecosystem is often determined by the elements--radiation, absorption, reflection, conductivity, convection and

evaporation. And these are usually regarded as functions of the four basic environmental variables, namely temperature, wind, velocity, humidity and intensity of solar radiation. How do these four basic characteristics of the environment affect the energy balance of ecosystems, as described by the numerous transport variables noted above?

2. In terms of energy balance, consider such animal activities as location, pursuit, capture and consumption (basic stages of foraging). In each stage, what is the work involved? What is (qualitatively) the energy gained and/or lost? How might the equation of energy balance for the whole phenomenon of foraging look? Compare a filter feeder, a sit-and-wait predator, and a searcher. Who uses more energy, and why?

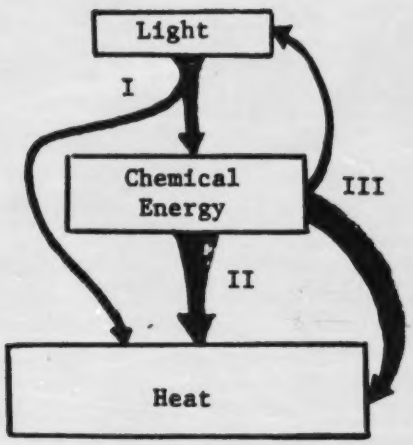
Neither of these questions are simple. They expect prior knowledge of transport processes and a sophisticated view of expected energy obtained versus expended in foraging. They are meant tc be thought- and question-provoking.

THE SECOND PRINCIPLE OF THERMODYNAMICS

The Second Principle of Thermodynamics (henceforth abbreviated SP) says that, in closed systems, thermal energy cannot flow spontaneously from regions with low temperature to regions with high temperature. It can be shown that equivalent statements of the SP are as follows: heat cannot be completely transformed into work, or no real process is truly reversible. Notice that all three of the formulations are restricted to closed systems. One of the main thrusts of modern thermodynamics is the demonstration of its applicability to open systems, but in entirely different situations.

We will discuss this further in a while, but now let us clarigy the meaning of the SP.

Although all forms of energy are capable of performing work with the associated necessary losses in the form of heat, all forms of energy may be converted completely and efficiently into heat but incompletely into other forms of energy. When higher-rank energy is transformed into lower-rank energy, there is no adequate way back to return the system to the initial state (see Fig. 1).



I Photosynthesis
II Oxidation
III Bioluminescence

Figure 1. Transformation of energy in biological processes.

Thus, light may be converted into chemical energy as is the case in the process of photosynthesis, but this process inevitably produces heat. And again, when chemical energy is transformed into light in luminoforous bacteria, for instance, a significant amount of heat is a natural co-product. It follows that, if heat is a "waste product" of an energy expenditure,

we cannot obtain equivalent work form it in an "irreversible world." Thus, if we start with heat, we can obtain work only by reducing the temperature of the system. Mechanical energy (work) has a higher rank than heat. The high temperature of steam in a steam engine may be used to produce work, but it also produces regions with lower temperature which makes the whole process irreversible. To reattain the initial temperature, we would have to spend more work than was obtained from the engine. Otherwise, we could produce some useful work, return the system into initial state without spending energy, then produce some work again and so on. In other words, the SP states that reversible processes cannot produce work, i.e., perpetuum mobile (perpetual motion, or an engine that works forever without refueling) is impossible. Thus, an application of the SP implies that, for any physical machine or body, the energy input must always be larger than the output and the difference is lost in a form of lower-rank energy (usually heat). The degree to which a given amount of energy is dissipated as heat is a measure of the irreversibility of the process.

The amount of waste heat produced in any thermodynamic process equals the entropy of a system times the (absolute) temperature at which the process takes place, that is, in differential form, from (2):

$$dQ = \theta dS \quad . \tag{17}$$

The more energy is dissipated as heat, the higher the entropy of the process at constant temperature. The SP asserts that, in closed systems, there is always heat production, unless the process is truly reversible and can really go in both directions, in which case the entropy change would be zero. In either case, entropy does not ever decrease with time in a closed system. Thus, the net change in the entropy content of the system between any two

states separated by a certain time interval dt is non-negative:

$$dS \geq 0 \quad . \tag{18}$$

The equality in (18) holds only for reversible processes in closed systems. It has been shown in classical thermodynamics that the change in the entropy of closed systems depends only on the end points (the initial and final state) and does not depend on the intermediate stages of the process (see, e.g., Abbot and Van Ness, 1972). Therefore, if the end points differ (the system did not return to its original state), the increase in entropy is the same whether the process is reversible or not. However, if the end points are the same, the entropy change for a reversible process is zero, while for an irreversible process it is greater than zero. This important conclusion may be clarified by an example.

Example: If a reversible process is accompanied by a change in temperature (from θ_1 to θ_2), then the expression for entropy (S) measured in e.u. = cal/degree Celsius per unit mass is

$$\text{at constant pressure, } \Delta S = c_p \ln \frac{\theta_2}{\theta_1} \tag{19a}$$

$$\text{at constant volume, } \Delta S = c_V \ln \frac{\theta_2}{\theta_1} \tag{19b}$$

where c_p is the specific heat capacity at constant pressure; c_V is the specific heat capacity at constant volume. Both c_p and c_V are known and tabulated for many substances (see, e.g., CRC Standard Handbook for Mechanical Engineers, McGraw-Hill, any edition).

Suppose we want to calculate the entropy change in the process of mixing 1 kg of water at 373 K (100°C) with 1 kg of water at 273 K (0°C)

under conditions of constant pressure. The resulting equilibrium temperature is 323 K (50°C). The process is, of course, irreversible, but for the moment consider it a reversible process with the system returning to the same initial and final states.

Process I: When 1 kg of water is heated from 273 K to 323 K, the entropy change is

$$\Delta S_I = 10^3 \times \ln \frac{323}{273} = 168.18 \text{ e.u.}$$

since $c_p = 10^3$ cal $kg^{-1}k^{-1}$ for water under constant pressure

Process II: When 1 kg of water is cooled from 373 K to 323 K, the entropy change is

$$\Delta SII = 10^3 \times \ln \frac{323}{373} = -143.93 \text{ e.u.}$$

For Processes I and II combined, the net change in entropy of the water is $\Delta S_I + \Delta S_{II} = 168.18-143.93 = 24.25$ e.u. for both reversible and irreversible processes, since the end points are not the same for either Process I or Process II. In Fig. 2, Process I goes from point A to point B (straight line) and results in positive net change in entropy. Process II goes from C to B and results in decrease of entropy. We don't care whether the process is reversible or not: the change in entropy is determined by the

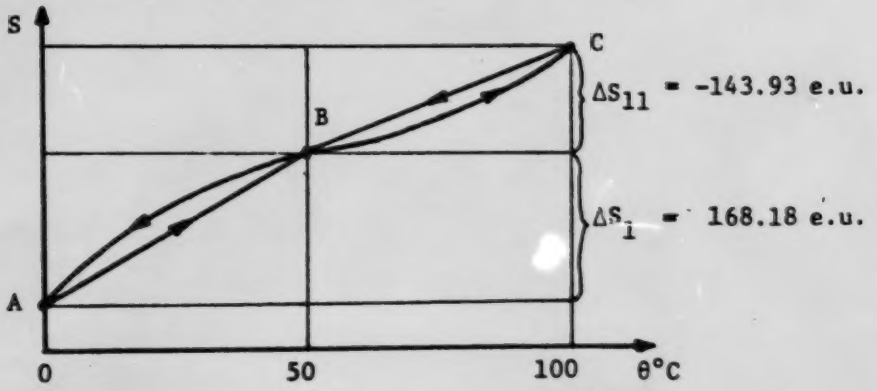


Figure 2. Entropy change in the process of mixing water (see text).

differences (B-A) and (B-C) on the entropy axis for Processes I and II, respectively.

In the reversible case, however, we had to use heat reservoirs (say, a stove and a refrigerator) to store the heat when the water was cooled or to extract the heat when the water was heated, just to make it possible to run and reverse the process. Just think about it: how can we reverse the process? We have 2 kg of water at 323 K and want to restore the initial situation with 1 kg of water at 273 K and 1 kg at 373 K. Therefore, we have to separate the water into two equal parts, heat one part (on a stove) and cool another part (in a refrigerator). These reservoirs are to be included in the system and the change in entropy of the reservoirs is equal and opposite to that of the water (curved lines on Fig. 2), the net entropy change being zero, simply because the end points of the process are the same (Process I goes from A to B for water and back from B to A for a stove that heated this water). That is to say, while the entropy of the water in Process I <u>increased</u> by 168.18 e.u. and that of the water in Process II <u>decreased</u> by 143.93 e.u. (total entropy of the water <u>increasing</u> by 24.25 e.u.), the entropy of the stove <u>decreased</u> by exactly 168.18 e.u. and that of the refrigerator <u>increased</u> by 143.93 e.u. (the total entropy of both the stove and the refrigerator <u>decreasing</u> by 24.25 e.u.).

On the other hand, if the process is irreversible, we do not need external appliances to store the heat. We just let the cold and hot water mix together and the cold portion uses the heat of the hot one, so that heat does not leave the water while the entropy increases (by 24.25 e.u.), thus contributing to the net increase in entropy of the universe.

<u>Exercise</u>: Suppose we start with 2 kg of water at 323 K and our intention is to reproduce the original state of 1 kg at 373 K and 1 kg at

273 K. What is the change in entropy of water if the process is (1) reversible? (2) irreversible? How did the entropy of the universe change if the process is (3) reversible? (4) irreversible?

The reader should note that in the foregoing discussion, as well as in the example, we were talking about closed systems. Our conclusions are applicable to isolated systems as well, but when we turn to open systems, the situation changes quite a lot. In closed systems, as we already know, there is a degradation of energy: the overall rank of energy is decreasing during any process. In open systems, there is a degradation of both energy and matter. Organisms utilize high-ranking energy (sunlight, chemical reactions, etc.) to do biological work, and exactly as it is with the closed systems, a large portion of this energy is wasted in the form of heat. Since the definition of an open system requires energy and/or mass flow, the existence of an energy flow implies an energy source and an energy sink where some portion of the initial energy goes in the form of waste heat. Thus, the definition of an open system implies degraded energy. We see that in a living open system, as well as in a physical closed system, irreversible chemical and mechanical processes typically produce heat. The only difference that we have noticed so far between open and closed systems is that the reversibility of a process is conceivable as an idealization in the framework of closed systems but is totally inapplicable to open systems. However, a more fundamental difference may be observed between these two types of systems when we turn to discussion of the entropy function and entropy production, owing to the fact that an open system's boundary is open to mass transfer. A possible application of the SP to open systems is as follows (Prigogine, 1947):

The net entropy change dS of any system during an arbitrary time interval dt is composed of two terms:

$$dS = d_e S + d_i S \tag{20}$$

where $d_e S$ is the change in entropy in dt owing to flow through the boundary (that is, owing to exchanges with the external environment), and $d_i S$ is the entropy production in dt resulting from internal processes.[3] For example, $d_e S$ may represent processes of radiation, conduction and convection, while $d_i S$ may be caused by diffusion or chemical reactions. The second principle states that, for a closed system, the total entropy change dS must be greater than zero, which means in closed systems the entropy function <u>increases</u> with time.

Consider the following: What is $d_e S$ for an isolated system? Evidently, it is zero, because there is no energy exchange with the system's surroundings. Three special cases may be distinguished.

1. When $d_i S = 0$, the entropy related to internal processes S_i has a constant maximum value. This is a condition for a thermodynamic equilibrium in a closed or isolated system, when processes are reversible. For irreversible processes, $d_i S > 0$, and so for a closed system, we have $d_i S = dS - d_e S > 0$.
2. When $dS = 0$, the total entropy of the system is constant. This situation may occur when $d_e S = -d_i S$, that is, there are flows through the boundary but they are compensated by internal processes. Since, for the internal processes, $d_i S \geq 0$ according to the SP, the flow through the boundary must help to neutralize the internal entropy increase, that is, $d_e S \leq 0$. This state can be achieved only in open systems owing to the

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[3] It is a convention in irreversible thermodynamics to put indices e and i immediately after the differentiation sign and not after the variable that is being differentiated (S). The underlying reason is that, in general, only the <u>net</u> change in entropy dS can be expressed as total differential while $d_i S$ and $d_e S$ may not be such, that is, they may not be expressible as total differentials with respect to independent variables. For example, $d_i S$ and $d_e S$ may not be independent.

inward transport of low-entropy matter. The situation $dS=0$ corresponds to a steady state which is common to all living biological systems. To reiterate--in a steady state, $d_eS=-d_iS<0$, while in equilibrium state, $d_iS=0$.

3. When $|d_iS| < |d_eS|$ and $d_eS<0$, or equivalently, $dS<0$, the total entropy of the system decreases with time. Many have argued that this is the case for a growing organism for which the inflow of low-entropy food tends to decrease the overall entropy level in the organism. It might be well to pause here to describe roughly the motivation for this point of view. Consider an open system (a growing organism) together with its environment. The total differential change in entropy is $dS=dS_1+dS_2$ where dS_1 and dS_2 are the total differential changes in entropy of the open system and the environment, respectively. As we know, $dS=d_iS+d_eS$ for the total supersystem, including the system and its environment. We may also write $dS_1=d_iS_1+d_eS_1$ and $dS_2=d_eS_2$ where $d_eS_1+d_eS_2=d_eS$ (see Fig. 3).

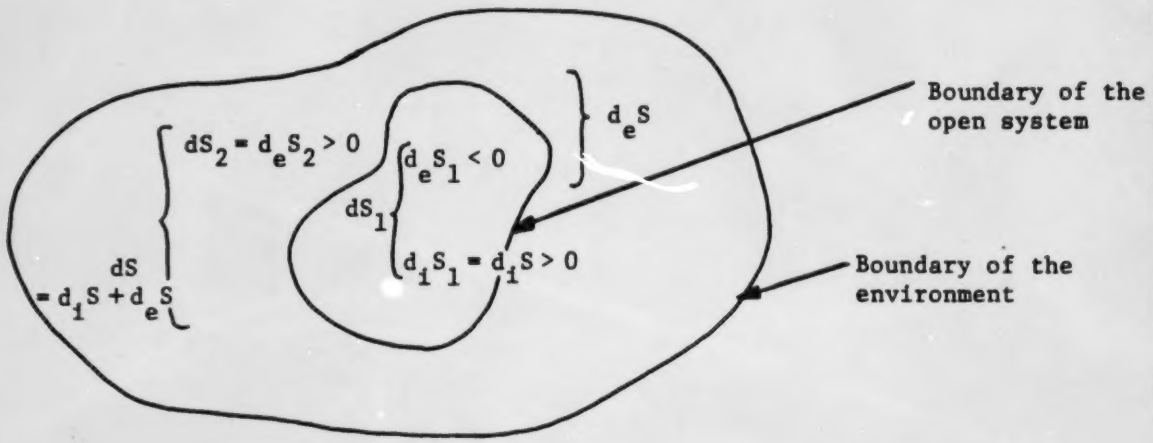

Figure 3. Entropy distribution in a typical open system.

By the SP, $dS \geq 0$ and $d_iS > 0$ while both dS_1 and d_eS_1 may be negative. If $d_eS_1 < 0$ and $|d_eS_1| > d_iS_1$, we have for the case $dS_2 > 0$

$$d_iS_1 + d_eS_1 = dS_1 < 0 < dS_2 - d_eS_2$$

that is, there is an entropy flow from the open system to its environment through the boundary. It should be noted here that we just discussed an example where d_iS and d_eS may not be represented as a linear combination of total differentials of independent variables because

$$d_iS = dS_1 - d_eS_1$$

$$d_eS = dS_2 + dS_1 - d_iS = dS_2 + d_eS_1$$

and here d_eS_1 may not be a linear function of differentials of independent variables. Think about it and recall the mathematical definition of the total differential (see Appendix).

In terms of (10), the entropy production is now redefined as

$$P = d_iS/dt \tag{20a}$$

while the quantity $\Phi = d_eS/dt$ receives the name of <u>dissipation function</u>. In the state of equilibrium, $P = 0$ whether the system is isolated or not. One of the main achievements of irreversible thermodynamics is the so-called Prigogine's theorem, or the principle of least entropy production; viz., when certain conditions are satisfied, in steady states close to equilibrium in open systems, $dP/dt = 0$ and P is minimal or least (not equal to zero, but slightly greater than zero). However, for nonlinear open systems far from equilibrium, a situation may exist when the entropy production actually increases. In living systems, these two kinds of behavior complement one

another. We now turn to the proof of the Prigogine's theorem. However, in a first reading or if a reader is not interested in the sketch of the proof, the main narrative about irreversible thermodynamics resumes with the discussion of Prigogine's theorem for a living organism.

PRIGOGINE'S THEOREM: THE PRINCIPLE OF LEAST ENTROPY PRODUCTION

The modern thermodynamics owes its momentum to the works of Ilya Prigogine, a Belgian scientist who was recently awarded a Nobel Prize in chemistry for important contributions to our understanding of irreversible processes in open systems. The major theorem proved by Prigogine and bearing his name opened new dimensions in thermodynamics and made it possible to understand why open systems tend to minimize their entropy (Prigogine, 1959). We will discuss this on the basis on two simple examples with the intention of supporting in a more rigorous way what has been presented in general terms in earlier sections.

According to Prigogine's theorem (Prigogine, 1947), when certain assumptions are valid, an open system in a steady state near equilibrium produces the minimal amount of entropy, since the entropy production decreases in the course of the system's evolution to this steady state. To prove this theorem, let us star with a review of some basic formulations. As we know from (4), (5) and (20), the differential change in system's entropy can be represented in its most general form:

$$dS = \frac{dQ_1}{d\theta} + \frac{dQ_2}{d\theta} + \Sigma s_i m_i = d_e S + d_i S \quad .$$

The entropy production, P, is related to entropy produced by the system and

is defined as

$$P = \frac{d_i S}{dt} \quad .$$

Now consider three cases.

1. In isolated systems, there is no heat or mass exchange with the surroundings, and therefore $\frac{dQ_1}{dT} = \Sigma s_i m_i = 0$, so that $dS = \frac{dQ_2}{dT} = d_i S$ and $P = \frac{dS}{dt}$. From a previous discussion (p. 26), in a state of thermodynamic equilibrium, there is no entropy change, that is, $dS = 0$, so that $P = \frac{dS}{dt} = 0$.
2. In a closed system, $dS = d_e S + d_i S$ with $d_i S \geq 0$ and $P = \frac{d_i S}{dt} \geq 0$. Again, in the state of equilibrium, $d_i S = 0$ and $P = 0$. It follows that for both isolated and closed systems, the entropy production in the state of equilibrium is minimal (zero).
3. In open systems in steady states, the entropy production P will not necessarily be zero. However, under some conditions, as specified below, P will reach its minimal value. If the open system is in a steady state close to equilibrium, we may employ the so-called local equilibrium assumption which postulates that any state of local non-equilibrium is described by the same variables and is governed by the same equations of state as those applicable to an equilibrium state (Glansdorff, 1977). Now we can start with the proof of Prigogine's theorem for open systems (we have to show that in a steady state $dP = 0$ and $P =$ minimum).

Prigogine's Theorem for Coupled Chemical Reactions

For the sake of simplicity, let us limit our discussion to the case of just two coupled chemical reactions with a constant supply of raw

materials and represent the reaction in matrix form:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

where a_{jk} is the k^{th} chemical component of the j^{th} reaction. For example, reaction 1 may be the reduction of acetaldehyde by NAD^+ in micro-organisms with ethyl alcohol as a product, while reaction 2 can be the 2,3 butylene glycol oxidation to acetylmethylcarbionl, as illustrated on Figure 4.

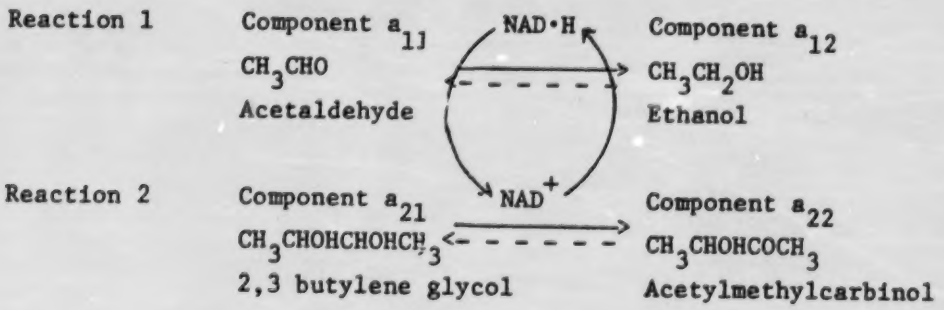

Figure 4. An example of a chemical open system (coupled chemical reactions).

Reaction 1: $a_{11} \rightleftarrows a_{12}$ is possible only in conjunction with reaction 2: $a_{21} \rightleftarrows a_{22}$. Both reactions 1 and 2 are assumed here to be reversible, although in practice reversibility is not strictly possible. However, when the system is open and there is a sufficient supply of chemical components a_{11} (in this case, acetaldehyde) and a_{21} (2,3 butylene glycol), both reactions go in the direction indicated by the solid-line arrows.

Energy released in reaction 2 is used to enable reaction 1 through the reduction of oxidated NAD (nicotinamidadenindenucleotyde). A stationary

state arises when the system receives the components a_{11} and a_{12} from the environment while the components a_{12} and a_{22} are removed from the system. In other words, when the rates of supply and removal are equilibriated, a steady state may be achieved in which the concentrations of the elements within the system no longer vary with time. If this steady state occurs sufficiently close to an equilibrium state, in the sense that the state variables have about the same values for both, the system may be considered approximately linear (the interaction between system variables can be described in terms of linear relationships). For this particular situation, Prigogine's theorem is applicable and relatively easy to prove.

We may begin by letting the mass of substance a_{jk} be represented by m_{jk}. From analytical viewpoint (see any introductory course on the kinetics of chemical reactions, for example, Bull 1971).
The differential dm_{jk} of the mass m_{jk} of the component a_{jk} in a chemical reaction j in time dt can be expressed as

$$dm_{jk} = \nu_{jk} M_{jk} dy_j \tag{21}$$

where ν_{jk} is a stoichiometric coefficient, this being a coefficient preceding a component jk in a chemical equation of reaction j, taken with appropriate sign; M_{jk} is the molecular weight of the component jk expressed in grams; and y_j is the extent of the j^{th} reaction.

For our case of two coupled reactions, (21) can be expanded into

$$\begin{aligned} dm_{11} &= \nu_{11} M_{11} dy_1 \\ dm_{12} &= \nu_{12} M_{12} dy_1 \\ dm_{21} &= \nu_{21} M_{21} dy_2 \\ dm_{22} &= \nu_{22} M_{22} dy_2 \,. \end{aligned} \tag{22}$$

The number of moles n_{jk} of the jk^{th} component is computed as

$$n_{jk} = \frac{m_{jk}}{M_{jk}} \quad . \tag{23}$$

Consequently, (22) and (23) can be rewritten in terms of the differential change in the number of moles as

$$dn_{jk} = \nu_{jk} M_{jk} dy_j \tag{24}$$

and

$$\begin{aligned} dn_{11} &= \nu_{11} dy_1 \\ dn_{12} &= \nu_{12} dy_1 \\ dn_{21} &= \nu_{21} dy_2 \\ dn_{22} &= \nu_{22} dy_2 \quad . \end{aligned} \tag{25}$$

The velocity (flux) of reaction j is defined to be

$$v_j = \frac{dy_j}{dt} \tag{26}$$

and we can relate the flux v_j to the rate of change in number of moles of the component a_{jk} as follows:

$$\frac{dn_{jk}}{dt} = \nu_{jk} \frac{dy_j}{dt} = \nu_{jk} v_j \quad . \tag{27}$$

The next step is to express a differential change in entropy owing to internal processes in the system, $d_i S$, in terms of the fluxes v_j and other variables introduced above. Note that the internal entropy change for the system is composed of changes attributed to each of the components

$$d_i S = d_i S_{11} + d_i S_{12} + d_i S_{21} + d_i S_{22} \tag{28}$$

where $d_i S_{jk}$ is the internal entropy change due to jk^{th} component. By introducing the notion of chemical potential of the jk^{th} component, μ_{jk}, defined as

$$\mu_{jk} = \theta \frac{\partial S}{\partial n_{jk}} \quad , \tag{29}$$

we can represent (28) by the substitution of $d_i S_{jk} = \frac{1}{\theta} \mu_{jk} dn_{jk}$ as

$$d_i S = \frac{1}{\theta} (\mu_{11} dn_{11} + \mu_{12} dn_{12} + \mu_{21} dn_{21} + \mu_{22} du_{22}) \tag{30}$$

or, in general,

$$d_i S = \frac{1}{\theta} \sum_j \sum_k \mu_{jk} dn_{jk} \quad . \tag{31}$$

There is an obvious similarity to (16), which did not deal with interactions. Finally, using (29) and defining the so-called affinity A_j of the chemical reaction j by

$$A_j = -\sum_k \nu_{jk} \mu_{jk} \quad , \tag{32}$$

we can rewrite (30) as

$$d_i S = \frac{1}{\theta} (A_1 dy_1 + A_2 dy_2) \tag{33}$$

or, generally,

$$d_i S = \frac{1}{\theta} \sum_j A_j dy_j \geq 0 \quad . \tag{34}$$

The physical interpretation of the notions of chemical potential μ_{jk}, or

affinity A_j lies outside the scope of this module. The reader is encouraged to use supplementary sources (see, for example, Abbot and Van Ness, 1972). However, for the purposes of this presentation, it is sufficient to regard defintions (29) and (32) as useful changes of notation.

If the system were closed, for a total mass m_j of the j^{th} reaction, we would have, using (21),

$$dm_j = d\Sigma_k m_{jk} = dy_j \Sigma_k \nu_{jk} M_j = 0 \tag{35}$$

or

$$dm_1 = dm_2 = 0 \qquad \text{for } j = 1, 2, \tag{36}$$

since the law of conservation of mass holds. For such systems at equilibrium, there is no flow and $A_j = 0$ for each j and, consequently, $d_i S = 0$. This means that entropy function S has reached its maximum value.

For irreversible processes going on in either open or closed systems, the production of entropy per unit time is

$$P = \frac{d_i S}{dt} = \frac{1}{\theta}\left(A_1 \frac{dy_1}{dt} + A_2 \frac{dy_2}{dt}\right) = \frac{1}{\theta}\left(A_1 v_1 + A_2 v_2\right) \geq 0 \tag{37}$$

or, in general,

$$P = \frac{1}{\theta} \sum_j A_j \frac{dy_j}{dt} = \frac{1}{\theta} \sum_j A_j v_j = \frac{1}{\theta} \phi \geq 0 \tag{38}$$

where $\phi \equiv \sum_j A_j v_j$ is the dissipation function. Equation (28) implies

$$\phi = A_1 v_1 + A_2 v_2 \geq 0 \qquad \text{or} \qquad \sum_j A_j v_j \geq 0 \tag{39}$$

where the equality sign holds for the equilibrium state (closed system). However, since we are interested in an open system, $\sum_j A_j v_j > 0$.

If reaction 2 cannot take place alone, lacking sufficient energy, then $A_2 v_2 < 0$. To make this reaction possible, it may be coupled with reaction 1 so that (24) holds, when $A_1 v_1 \geq |A_2 v_2|$. For example, transport against a concentration gradient is possible when it is conjugated with other thermodynamically advantageous reactions to assure relationships as expressed by (39).

We now introduce the notion of a thermodynamic force F_j defined as

$$F_j = \frac{A_j}{\theta} > 0 \quad .$$

Examples of thermodynamic forces are temperature and chemical gradients.

It can also be shown that the condition of closeness to equilibrium is measured by

$$\left|\frac{F_j}{R}\right| \ll 1 \tag{41}$$

for each individual reaction j, where $R = 8.3 \times 10^7$ erg K^{-1} $mole^{-1}$ is a universal gas constant. If F is the thermodynamic force of the whole system, the condition (41) may hold even if $\frac{|F|}{R} > 1$. In other words, an open system is close to equilibrium if each reaction satisfies (41). Furthermore, it can be shown that (41) corresponds to the requirement of the linearity of the process.

For reactions close to equilibrium (for open systems, it may be a steady state in the neighborhood of thermodynamic equilibrium), the flux v_j is proportional to the thermodynamic force F_j with proportionality constant L

$$v_j = L \cdot F_j \quad . \tag{42}$$

Under the assumption of the linearity of the process, the expression (41) represents a linear relationship, in the sense that the proportionality coefficient L is a constant and the expressions entering (42) are not powers, exponentials or other nonlinear functions of the variables. For coupled reactions, the flux of each reaction is a linear function of thermodynamic forces. For example, if we have two coupled reactions, the flux of each reaction depends linearly on the force of the first reaction and the force of the second reaction:

$$v_1 = L_{11}F_1 + L_{12}F_2 \qquad (43)$$

$$v_2 = L_{21}F_1 + L_{22}F_2$$

or

$$v_j = \Sigma\, L_{jr}F_r \qquad (44)$$

so that the rate of entropy production owing to natural processes within the system is

$$P = \frac{d_i S}{dt} = \frac{1}{\theta}\,(L_{11}F_1^{\,2} + L_{12}F_1F_2 + L_{21}F_2F_1 + L_{22}F_2^{\,2}) > 0 \qquad (45)$$

or

$$P = \frac{1}{\theta}\sum_{j=1}^{n}\sum_{r=1}^{n} L_{jr}F_jF_r > 0 \quad . \qquad (46)$$

L_{jr} are called phenomenological coefficients and, under certain conditions, they satisfy the Onsager relations (Onsager, 1931):

$$L_{jr} = L_{rj} \quad . \qquad (47)$$

Using (47), the expression for entropy production (45) becomes

$$P = L_{11}F_1^2 + 2L_{12}F_1F_2 + L_{22}F_2^2 \quad . \tag{48}$$

Taking the partial derivatives with respect to either F_1 or F_2, we have

$$\frac{\partial P}{\partial F_1} = 2(L_{11}F_1 + L_{12}F_2) = 2v_1 \tag{49a}$$

$$\frac{\partial P}{\partial F_2} = 2(L_{22}F_2 + L_{12}F_1) = 2v_2 \quad . \tag{49b}$$

For the equilibrium state, fluxes are zero, so that the rate of entropy production is

$$\frac{dP}{dt} = \frac{\partial P}{\partial F_1}\frac{\partial F_1}{\partial t} + \frac{\partial P}{\partial F_2}\frac{\partial F_2}{\partial t} = 0 \quad . \tag{50}$$

By the local equilibrium assumption, (50) holds for the steady state close to equilibrium. Since the time derivative of P is zero, P has an extremum at this state, that is, $P = \frac{d_i S}{dt}$ in a steady state close to equilibrium reaches either a maximum or a minimum. It can be shown, for example, by taking the second time derivative of P, that the extremum achieved in this steady state is, in fact, a minimum, so that, as expected, the entropy production in a steady state close to equilibrium is minimal (but not necessarily zero).

Prigogine's Theorem for a Living Organism

As another example, consider a living organism in the conditions of stationary existence, that is, with approximately constant mass and parameters of the immediate environment. Such an organism uses the chemical energy of its food to maintain internal working processes and dissipates the same amount of energy in the form of a heat flux into the

external medium. The differential amount of work performed in the living system is

$$dW = \sum_{j=1}^{n} F_j dv_j \tag{51}$$

where F_j is a thermodynamic force and v_j is the velocity of the j^{th} process. According to Fourier's law, the heat flux $q = \frac{dQ}{dt}$ is proportional to the temperature gradient

$$\vec{q} \propto \text{grad } \theta \tag{52}$$

or

$$\theta \frac{dS}{dt} = \frac{dQ}{dt} = C \cdot B \ (\theta_o - \theta_e) \tag{53}$$

where C is the organism's coefficient of mean heat production, B is the area of the boundary of the system, θ_o and θ_e are the temperatures of the organism and environment respectively.

From (23), (25), (33) and (34), we have

$$\frac{dS}{dt} = CB(\theta_o - \theta_e) = \frac{dW}{dt} \ . \tag{54}$$

In a stationary state, the organism produces a constant amount of work in a unit time

$$\frac{dW}{dt} = \text{const} \ , \tag{55}$$

or

$$\frac{d}{dt} \left(\frac{dW}{dt}\right) = 0 \tag{56}$$

so that

$$\frac{d}{dt} \left(\theta \frac{dS}{dt}\right) = 0 \tag{57}$$

in accordance with Prigogine's theorem.

The reader should be aware that the mathematical and physics structure presented is valid but application to real systems always involves many assumptions. Applications to living systems, because of their great complexity are speculative at best, at present.

This theorem is only valid in the range of linear irreversible processes and with the assumption that Onsager relations (47) hold. Moreover, Prigogine's theorem as proved here is applicable only to steady states in the vicinity of thermodynamic equilibrium. As we know (see the discussion on dissipative structures earlier in this module), open systems may have steady states far from equilibrium. The system in these states may or may not exhibit an equilibrium-type behavior, and in the latter case the theorem would not apply.

Distance from Equilibrium, Stability and Nonlinear Domain

The problem of an open system's evolution toward a steady state was found to be related to the problems of stability. As we know, far from the equilibrium, certain open systems become unstable, as described on pp. 7-8 of this module. Distance from equilibrium, as defined by (41), is an important thermodynamic parameter characterizing the state of a system. The entropy production obeys Prigogine's theorem only if this distance is not very large and if the transport processes are approximately linear.

A new type of "generalized thermodynamics" has been developed in the past few years which is capable of solving many of the nonlinear, nonequilibrium problems (Glansdorff, 1977). For the nonlinear domain of processes in open systems far from equilibrium, the entropy production may be expressed as

$$dP = d_A P + d_F P \tag{58}$$

where $d_A P$ and $d_F P$ are the variations in P due to flows and thermodynamic forces, correspondingly. The principle of minimum entropy production is in this case reformulated as

$$\frac{d_F P}{dt} = 0 \quad .$$

Notice that, in general case, $d_F P$ may not be the total differential of independent variables. A systematic violation of the assumption of linearity in living objects does not invalidate the Prigogine's theorem. As S.R. Caplan put it: "Whether or not the systems are truly linear over the entire range of biological interest is frequently beside the point--the provision of a single coherent logical framework is much more important" (Caplan, 1971).

Finally, we mention an important inequality that can be regarded as a universal stability criterion for non-equilibrium states:

$$\Sigma \delta v_j \delta F_j \geq 0 \tag{59}$$

where δv_j and δF_j denote variations in flux and thermodynamic force of the j^{th} reaction.

ENTROPY VS. ORDER

We now move from solid physical and mathematical explorations into philosophical speculations. Much of the material that follows lacks the solid credibility of scientific knowledge: any connection between entropy

and order, information, life or evolution is still a conjecture lacking sufficient corroborative evidence. Although some of the hypotheses discussed appear to be well substantiated, they are not universally accepted by the scientific community.

Entropy and Probability

The relationship between entropy and probability in a closed ideal gas system is given by the famous Boltzmann formula:

$$S = k \ln W \quad . \tag{60}$$

Here, k is Boltzmann's constant = 1.38×10^{-16} erg/K and W stands for the thermodynamic probability of a given state, this being the number of all possible arrangements of system's elements that result in this state.[4] Now let us interpret this equation. Suppose you are given a box filled with gas. Then, at any particular moment, every molecule of this gas has some position and a certain velocity. In a three-dimensional space, both position and velocity will be determined by three coordinate values each, so that we can describe the gas by assigning six values to every molecule. If there are N molecules in the box, we need to know 6N numbers to determine the microscopic state of the gas. However, a macroscopic state of the same gas (with macroscopic parameters, such as temperature) depends on less than 6N parameters because it depends on the kinetic energies of the molecules rather than on the direction of their velocities. On the other hand, all the molecules in the ideal gas are the same, and therefore their random permutation will not affect the macroscopic picture. Following Boltzmann,

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[4]Do not confuse this W with work. It often in the case that the same symbol is used to denote entirely different entities owing to historical reasons. It rarely is confusing if viewed in context.

we may say that each macroscopic state may be realized by a certain number of complexions; that is, a certain distribution of kinetic energies and positions of individual molecules. Assuming that each complexion occurs with equal probability, we can define the thermodynamic probability W of a certain state simply as the number of complexions that permit this state to be realized by a permutation of molecules. Note that W may be and usually is greater than unity. To make this notion compatible with the usual mathematical probability, one has to divide W by the total number of possible complexions, say W_o, so that

$$p = \frac{W}{W_o} \tag{61}$$

where p is the mathematical probability of a given macroscopic state. In closed systems, W tends to increase with time up to a certain maximum known as the equilibrium state.

The concepts of entropy and probability are related to the concept of information. We have now briefly discussed the first step in developing the relationship that is said to exist between the thermodynamic notion of entropy on one hand, and the information content of a message, or a system, on the other hand. This is a remarkable interrelationship that may be very fruitful in the future development of science. We will see how these idaes can be used in various biological fields, including the intriguing applications in genetics, e.g., for DNA and RNA messages, etc. (Oster et al., 1974).

Entropy and Information

Mathematically, information content is defined as

$$I = - \log_2 p = 0.693 \ln p \tag{62}$$

where p is the mathematical probability of observing a system in a certain state or, say, getting a certain outcome in an experiment or getting a certain message. The $\log_2$ stands for the logarithm in the base 2. Information content is measured in units called "bits" (from binary units). One bit is the information content of a system that has just two equally probable states. When you throw a coin, the probability is .5 of seeing either "E pluribus unum" or "In God We Trust." So, whatever the outcome of the toss, the information obtained is

$$I = - \log_2 \tfrac{1}{2} = 1 \text{ (bit)} \quad .$$

Exercise: Your neighbor is expecting a baby. Finally, a message arrives: "A boy!" What is the information content of this message? Suppose the message reads: "A baby!" What is the information content of this message?

When several information-bearing elements of a system are present, the average information content per element is calculated as

$$I_{ave} = - \sum_{i=1}^{n} p_i \log_2 p_i \qquad (63)$$

where n is the number of elements and p_i is defined as in (62) for each element.

In ecology, the expression (63) and others like it are frequently used to describe species diversity (Plimpton, 1977), with p_i (i=1, ..., n) being the proportion of species i in a population of n different species. Thus, minimal average information corresponds to a minimum of rare species while maximum average information corresponds to maximal species diversity.

Example: Suppose you want to compare two forests using the information: the first forest has 30% birches, 30% aspens, and 40% pine trees. The second one has 70% birches, 10% aspens, 10% firs, and 10% oaks. An average information content per tree for the first forest:

$$I_{ave\ 1} = -(0.3\ \ln 0.3 + 0.3\ \ln 0.3 + 0.4\ \ln 0.4)/0.693 = 1.57 \text{ bits},$$

for the second forest:

$$I_{ave\ 2} = -(0.7\ \ln 0.7 + 0.1\ \ln 0.1 + 0.1\ \ln 0.1 + 0.1\ \ln 0.1)/0.693$$
$$= 1.36 \text{ bits}.$$

The second forest has more species but less average information per tree because the vast majority of trees are birches: When we enter this forest, the first tree that we can see gives us less information about the population than a tree in the first forest. We will discuss in greater detail various measures ("indices") of diversity and their possible relation to the problems of stability of populations in a companion module devoted to ecological applications.

The average information content has been roughly calculated for various objects and some of the estimates are given in Table VI.

Table VI. Average information content (in bits).

Letters of English alphabet (if each letter has an equal probability of being used	4.70
Same (for unequal porbability, same combinations of letters as in printed English)	2.76
Printed page	10^4
Telephone conversation	288,000

Table VI (cont.)

Gene	10^7
Germ cell	up to 10^{13}
Mature man	up to 5×10^{25}

The first value was calculated by a direct application of (63) as follows:

$$I_{ave} = -\sum_{i=1}^{26} \frac{1}{26} \log_2 \frac{1}{26} = 4.7 \text{ bits} \quad .$$

For the printed English, the average information per letter is smaller because letters are not combined randomly; some letters (like e) and combinations of letters (like th) occur more frequently than others, and so on. When appropriate probabilities are used in (63), the value 2.76 results. A very rough estimate of the essential information contained in the gene may be obtained as follows. Structural information in genetic material may be approximately equal to 2 bits per pair of nucleotides. A DNA molecule of a bacterial cell has about 10^7 pairs of nucleotides, so that the total information content is about 2×10^7 bits. To compute an average information content in a living cell, some very general considerations lead to the orders of magnitude of $10^{10} - 10^{13}$ bits (Quastler, 1964). Calculations start with information of 24.5 bits needed in order to fix a position of an atom in a living system. There are about 2×10^{11} atoms in a bacteria Escherichia coli, so that the upper limit may be estimated as $24.5 \times 2 \times 10^{11} \approx 5 \times 10^{12}$ bits. Limitations on the mutual orientation between molecules may reduce this value to 10^{10} bits.

However, these estimates are certainly overstated. A certain part

of structural complexity of a living cell is redundant. On the other hand, it should be emphasized that all these calculations are conditioned upon vulnerable assumptions. The information of the order 10^{13} bits may be sufficient to localize all the molecules in a bacterial cell; however, one should also take into account the actual place of each molecule; that is, the whole hierarchy of interactions among the system's elements. By the way, why should we start calculations with molecules rather than atoms or electrons?

Modern information theroy is widely used in many areas and especially in communications from where the term "noise" comes. When a message is transmitted, certain information may be lost owing to noise. This idea is generalized to any form of information: noise or losses simply mean degradation of information. It is clear that information which is being transferred within a single organism as well as between organisms and environment also may degrade. Structural information undergoes degradation owing to a spontaneous motion of atoms and molecules; information losses occur due to such diverse phenomena as aging, cancer, mutations, and pollution. However, in general, structural information in an organism increases as a result of development and is retained at an approximately constant level in a steady state in an adult organism.

Although the notion of information is without doubt very useful in life sciences, biologists are mostly concerned with the quality of information (e.g., the nutritional aspects of food or the quality of reproductive material) rather than its quantity. Information theory cannot yet provide us with these types of qualitative information analysis.

We now turn to the relationship that exists between information and entropy. In 1929, Leo Scillard postulated a reciprocal correspondence

between entropy and information based on the fact that the latter has the same mathematical expression up to the constant and sign. Let us discuss this correspondence in more detail.

Consider an ideal gas in equilibrium. We can measure its temperature or pressure but, as far as the location of individual molecules and their velocities are concerned, we are unable to say anything definite. This is a state of maximum entropy (because the thermodynamic probability W of equilibrium state is maximal; that is, the number of all possible positions and velocities of the molecules is infinitely large). This is also a state of minimum information because equilibrium is a stable state and p is close to 1 (since there is a very high probability that the system will arrive at and stay in this state). On the other hand, the same gas under the conditions of very low temperatures (close to zero Kelvin) would have a crystalline structure with every molecule holding its own place. The number of possible microscopic states W is then close to one and entropy is close to zero. However, our information about the system's state is maximal: we actually know which state the system is in, while the probability that the system is (spontaneously) in this state is extremely low. In general, the greater our uncertainty about the microstate, the higher is the entropy of the system.

Thus, entropy and information flow in opposite directions: if the system's entropy is increased, its information content is decreased. Since information content is associated with the system's orderliness, entropy may be regarded as a "measure of disorder." It should be remembered that the above discussion and conclusions were based on a simple analogy between two mathematical expressions; this is an example of how "pure reasoning" may lead to new dimensions in science. For a comprehensive anthology of

recent papers on entropy and information in science and philosophy, see Kubat and Zeman, 1975.

Example: A famous illustration of the problems discussed above is the formation of crystals. A sodium chloride crystal is an orderly structure which is created out of a disorderly substrate (a saturated solution). It grows and reproduces itself and thus exhibits characteristics which are essential for living systems. Yet it contains very little information and it is not alive. The point is that crystal is the most probable state of the system which consists of sodium chloride and water. Hence it is in a state of maximum entropy and has minimum free energy. The probabilistic aspect contributes more to the net gain in entropy than the (relatively small) increasing information about the system's microstate.

To show the relationship between entropy and information more vigorously, let us consider (62) again to show its similarity to (60). In (62), p is commonly defined as

$$p = \frac{\text{\# of favorable outcomes, or choices, } P_1}{\text{total \# of possible outcomes, } P_2} \tag{64}$$

so that (62) takes the form

$$I = 0.693\ (\ell n\ P_1 - \ell n\ P_2) = 0.693\ \ell n\ \frac{P_1}{P_2}\ . \tag{65}$$

P_1 and P_2 may be looked upon as the number of choices between the system's states before and after the obtaining of information I from the system, respectively. On the other hand, a gain in entropy may be expressed as

$$\Delta S = S_2 - S_1 = k\ \ell n\ W_2 - k\ \ell n\ W_1 = k\ \ell n\ \frac{W_2}{W_1} \tag{66}$$

where W_1 and W_2 are the thermodynamic probabilities (= numbers of possible states) of the initial and final states of the system, respectively. Here k is Boltzmann's constant as in (60).

To make S and I comparable, let us change the scale so that the constant premultiplying the logarithms in (65) and (66) is the same, say K'. Consequently, we may rewrite (65) and (66) as

$$I = K' \ln \frac{P_1}{P_2} \tag{65a}$$

$$\Delta S = K' \ln \frac{W_2}{W_1} \quad . \tag{66a}$$

It is evident that $P_1 = W_1$ and $P_2 = W_2$ since the number of choices between the system's states corresponds to the number of possible states. Thus

$$\Delta S = -I \qquad \text{or} \qquad I = -\Delta S = S_1 - S_2 \quad . \tag{67}$$

In other words, an entropy increase corresponds to losing information, or gain in information corresponds to entropy decrease.

Example: Suppose you want to investigate a particular ecosystem which you know nothing about. That means your initial information is zero, $I_1 = 0$. Let us define the set of ecosystem's possible states as succession, climax, senescence, and maybe, a couple of intermediate situations. After a series of observations, you come to the conclusion that senescence and the other states that are connected with the system's degradation should be excluded from consideration. Thus the information that you obtained on the basis of observations reduced the number of the ecosystem's possible states from P_1 to, say, P_2, so that $I_2 = K' \ln(P_1/P_2)$. Initially, the entropy of the system was $S_1 = k' \ln P_1$. After observations, the entropy was reduced

to $S_2 = k' \ln P_2$. It turns out that

$$I_2 = S_1 - S_2 \quad \text{or} \quad S_2 = S_1 - I_1 .$$

Therefore, information that we collected about the system was possible owing to the decrease in the system's entropy (notice that the observer was included into the system).[5] This leads to the very important notion of negentropy.

Negentropy and Life

Brillouin (1964) introduced the term "negentropy" to specify a quantity $N = -S$. The famous negentropy principle of information says that any additional information increases the negentropy of the system. Any experiment with or inquiry about the object system transforms some of the entropy into information about the system, and information is a negative contribution to the system's entropy. Negentropy is thus synonymous to information while entropy may be called a "neginformation," or disorder.

"The organism feeds on negative entropy" (Schrodinger, 1945). This means that, due to metabolism, the living organism avoids the equilibrium which corresponds, as we know, to maximal entropy. To compensate for its own entropy production, the organism gets negentropy from the ambient media through the exchange of matter and thus delays equilibrium (death). This is

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[5]Some authors use the term "entropy" for average information, and inevitable confusion results. However, this usage may be justified as follows. Average information is in a sense a measure of uncertainty because the degree of diversity or complexity of a system corresponds to a plurality of choices between the system's possible states. The more choices you have, the more uncertain you are about a particular choice and the less information you have about the system. In other words, more information in the system corresponds to less information of an observer. For the purpose of this module, we will limit the term "entropy" to the conventional usage; that is, a negation of information.

possible because food usually contains less entropy and more information than metabolic wastes. An adult organism keeps the amout of its energy and substance relatively constant, so that the primary role of metabolism (says Schrodinger) is the intake of negative entropy. It is not the amount of energy in food that we are primarily interested in. It is the nutritional value of the meals; that is, the higher rank of energy and the negentropy of different substances.

But the other side of the coin is that, while consuming negentroyp, an organism discards its entropy in waste products as well as by direct dissipation of heat. In other words, the accumulation of negentropy in living systems corresponds to increasing entropy in the ambient media. For example, the ecosystem energy wastes are passed off to decomposers and ultimately dissipated as heat while the entropy of wastes is passed on to the environment. Since that is the case for both a single organism and an ecosystem and even a human society, it is the principal reason for thermal and material pollution (for more details about the thermodynamic aspects of pollution, see the companion module). Some authors suggest (Sacher, 1967) that there is a direct relationship between the rate of entropy production and the rate of aging. Thus aging can be viewed as a result of the increase in organizational entropy.

To summarize, any biological system acts as if "entropy is pumped" outward as "information is pumped" inward. That allows organisms to increase their information content and, consequently, their structural complexity and orderliness. Thus, it seems that living systems disobey the SP which is a universal law in the non-living world. This has been a crucial point in many discussions and opinions differ. Some authors think that an increase in entropy of the surroundings of an organism is much larger than

the corresponding decrease of the entropy in the organism itself. Living creatures, they say, are just "isles of increasing negentropy in the ocean of increasing entropy;" they can temporarily help to slow down the process of "thermal death" of the universe, but they cannot reverse it, so that the total entropy of the organism (or biosphere) and its environment increases in accordance with the second principle. Several objections to this point of view may be presented on the basis of general considerations:

1. Even if the accumulation of negentropy in structural organization of individual organisms is temporary (i.e., until death) the total accumulation of negentropy in the earth's biosphere increases with evolution, as we shall see below.
2. Human society on earth shows certain indications of a progress that goes in the direction of decreasing entropy. Compared with the energy wastes and entropy increase in society due to its mere existence, the entropy balance for man might be negative.
3. How much is a single sonnet of Shakespeare worth in terms of negentropy --who can calculate the value?

These and other considerations do not prove anything and we mentioned them here only to demonstrate the scope of the problem.

In order to complete our general discussion of entropy-related phenomena, we should briefly mention the relationship between entropy and time.

Time's Arrow

In 1929, Eddington introduced the notion of "time's arrow" which he defined by increasing entropy. It seems that time flows in one direction only, namely, from the past to the future, and cannot go back. It is the

irreversibility of physical processes that gives time its direction.

In our universe, only three entities are known to possess such a unique property as the direction irreversibility: entropy, time and the universe itself (c.f. the phenomenon of the expanding universe). Life and organic evolution sometimes are also considered as the examples of irreversibility of time. After Einstein, the time's arrow was connected with the maximal speed of the distribution of a signal. This interpretation is applicable to all levels of scientific investigation, while the thermodynamic considerations are true for macroscopic phenomena only (Zeman, 1971).

Paradoxically, the fundamental problem of both classical and irreversible thermodynamics lies in the fact that the equations proposed to describe the entropy function do not contain time explicitly. It is understood that the entropy function is nondecreasing in the physical world and moreover that entropy increases nonlinearly with time. Several attempts have been made to introduce time as an explicit variable on which entropy depends exponentially, but these attempts have failed to gain unanimous support in the scientific community (Reik, 1953).

Exercises

1. Reformulate the second principle and its consequences in terms of negentropy.
2. (Morowitz, 1971.) Consider two boxes, each one having exactly one molecule labeled A and B, floating freely within the boundaries, as in Fig. 5 (State I). Suppose next that the partition between boxes is removed (State II). Which state has a higher entropy? Base your answer on your knowledge (information) about where the A and B molecules actually are.

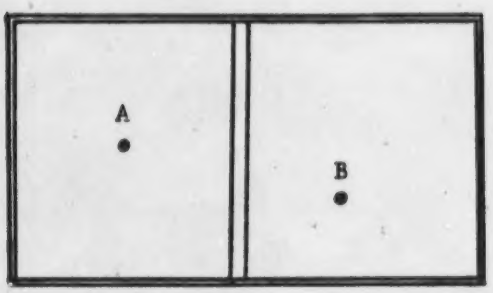

Figure 5. Boxes with molecules A and B of exercise 2.

3. (Patten, 1959.) It has been shown that certain ecological communities consume as much as 3×10^{24} bits/cm^2 per year of negentropy (Odum, 1957). How many pages should there be in a book that describes the annual information requirement on a square centimeter of area in such a community?

IRREVERSIBLE THERMODYNAMICS AS APPLIED TO THE PROBLEMS OF THE ORIGIN OF LIVE AND EVOLUTION

In this section, we shall discuss briefly some of the possible biological applications of the principles of irreversible thermodynamics. It should be emphasized that the main effort in the thermodynamic interpretation of biological phenomena is put on explanation of how structures differentiated in time and space can originate from less structured systems. Scientists are interested in chemically reacting open systems that at some point exhibit orderliness and a tendency to evolve. We will limit our discussion to the general levels of scientific inquiry where the same patterns are sought: namely, the origin of life and evolution.

The Origin of Life

If life in an ordinary phenomenon coming about as a result of the laws of the universe, what thermodynamic arguments explain its origin? It can be shown that the formation of asymmetric molecules (such as protein) by chance requires more space and time than our Einsteinian universe can offer. Quastler (1964) arrives as a probability of 10^{-255}. Even if we take for granted that protein was formed from existing amino acids, or DNA from the mononucleotides present in primordial "broth" rather than from separate atoms, still it is almost impossible to associate amino acids or nucleotides into a polymer by random combination of molecules (Yockey, 1977). Therefore scientists are still looking for other possible explantions of the origin of lie, and irreversible thermodynamics provides a basis for discussion.

TABLE VII. Comparative time table in billions of years (after Shapley, 1958)

Age of the universe	10
Age of the stars	5
Age of the earth	3-4.5
Age of the biosphere	2.5

Let us look at a comparative time table. The earth is about 4.5×10^9 years old, while chemical evolution presumably began about 3×10^9 years ago (Table VII). The atmosphere rich in oxygen as a characteristic of life was created about one to two billion years ago. Conditions that made life possible included a highly concentrated solution of relatively simple molecules and rich sources of energy, such as ultraviolet

light, ionizing radiation, thermal quenching and electric discharges (Ozo and Miller, 1977). This was an open system and therefore the laws of irreversible thermodynamics were applicable. At present, practically all monomers of the important biocolloids, including amino acids, have been obtained from simple precursors in laboratories in an attempt to reproduce the conditions that might have existed on earth a couple of billion years ago (Ozo et al., 1974). From homogeneous chemically reacting systems of bionomoners, the so-called dissipative structures (evolving and structured open systems that dissipate heat) could have been created.

We have seen that dissipative structures may be formed in open systems beyond a critical distance from equilibrium, provided that the processes in these regions exhibit intrinsic nonlinearity and the arising steady states are unstable. Beyond the stability threshold (which corresponds to the critical distance from equilibrium), many nonlinear open chemical systems become spontaneously inhomogeneous and show a spatial or temporal distribution of chemical components. Sometimes the concentrations of chemicals may oscillate in a sustained fashion.

The same phenomena may be found in living systems. It has been shown that metabolic processes in early embryogenesis, as well as in some stages of growth, are associated with a fast rate of heat dissipation. Such an increase in heat dissipation and a corresponding increase in entropy production is possible for nonlinear living systems in the states far from equilibrium. This situation, through a sequence of unstable transformations, may lead to spatial and temporal order in the system.

In a contrast to equilibrium systems, organization in a dissipative structure such as a thermodiffusion cell, in which a flow is maintained by a gradient or concentration, gradually increases owing to the dissipative

process of heat exchange. The organizational structure would be proportional to the increase of the temperature of concentration gradient. This, in turn, may lead to the creation of highly complicated organic compounds compatible with our definition of life (Prigogine, 1959). Let us discuss how this description may be applied to a system containing mononucleotides and amino acids.

Polynucleotide polimerisation in an open system under normal conditions reaches a steady state in the neighborhood of thermodynamic equilibrium with a small polymer concentration. By adding monomers, the distance from equilibrium increases and this leads to a sharp increase in the polymer-to-monomer ratio due to a template action (a nonlinear process!), giving rise to a dissipative structure. Under the conditions of a constant supply of monomers (nonequilibrium, the population of biopolymers exhibits energy metabolism, autocatalytic properties and a reproduction capability. Proteins play a role of catalysts that couple different template mechanisms. When errors occur in replicating a certain type of polymer, usually due to thermal fluctuations, a polymer of a new type may be produced. Eventually, one of the error copies may even serve as a template for the synthesis of a substance which, in turn, catalyzes the production of this error type.

If the total concentration of reacting polymer types ("species") is somehow limited, a favorable error ("mutation") may be propogated due to the nonlinearity of the template reactions at the expense of other types ("selection"). Here errors may be thought of as fluctuations that lead the system to a new steady state far from equilibrium. A system will evolve further only if this new state is unstable. Therefore evolution will tend to produce species of polymers that are most stable with respect to fluctuations. This is a modern thermodynamic interpretation of the old

principle of the "survival of the fittest" as applied to prebiological evolution (Prigogine, Nicolis, Babloyantz, 1972).

We have discussed that the minimum dissipation principle (Prigogine's theorem) holds under condtions where the system is not very far from a stable steady state which is in the neighborhood of equilibrium. In contrast, beyond the transition threshold, as evolution proceeds from an old steady state to a new one, the system tends to increase its dissipation (entropy production). In other words, dissipation increases during the transient stage when a mutation causes the production of a new species. These two types of behavior, far and close to equilibrium, complement each other. To summarize, in prebiological evolution, dissipative structures may have arisen from a homogeneous mixture of mononucleotides and amino acids. These structures were associated with the increased entropy production (heat dissipation) and a certain orderliness. They evolved through a regulated sequence of instabilities in the direction of increasing nonlinearity and the distance from equilibrium. Every organism exhibits such a behavior on early embryonic states and is later complemented by another form of behavior which is associated with the minimum of entropy production. This explanation of prebiological evolution has been proposed and developed by I. Prigogine and other representatives of the Brussels school (Prigogine, 1959; Prigogine, Nicolis and Babloyantz, 1972; Glansdorff and Prigogine, 1974; Glansdorff, 1977). Still there are alternative hypotheses about the origin of life.

The Russian biophysicist K. Trincher (1965) suggested that, since the age of the living matter is of the same order of magnitude as the age of the expanding universe (10^9 - 10^{10} years), the same conditions which gave rise to the expansion of the universe may be responsible for the emergence

of life. Life was born on earth, seemingly, like a thermodynamic phase which occurred suddenly upon a sudden change in the physical conditions--not as a single molecule capable of reproduction but as a biosphere.

In any case, once a highly structured system of molecules capable of reproduction emerged on earth, they exhibited a strong tendency to increase their organization. Early forms of life shared that unique capability of all open systems to evolve in the direction of ever increasing complexity. This brings us to the phenomenon of evolution.

Evolution vs. Entropy

Living systems may be said to be in a state of continuous and irreversible evolution. According to Dollo's Law (see Petronievics, 1918), an organism cannot return, even in part, to a previous condition passed through in the series of its ancestors. Evolution is irreversible as regards the structure and functions of organisms, even if it is reversible as regards environment. Evolution may be, as we know, progressive, regressive, or mixed. Organs or parts of organs reduced or lost through regressive evolution cannot be regained by a new progressive development. Eventually, if the original structure of an organ has been lost through an ascending evolution, it cannot be regained by regressive evolution of the new parts or by development of these new parts in a new direction. Considering Dollo's Law in thermodynamical retrospective, one meets the difficulty of defining a system where the entropy change between two phylogenetic states occurs. But whatever the definition may be, the irreversibility of evolution has an appealing familiarity to the laws of irreversible thermodynamics--both perhaps being manifestations of fundamental principles of the universe (Blum, 1962).

The present concepts of evolution are based on two essential phenomena: mutations and natural selection. Our purpose will be to show that these concepts undoubtedly can be connected with thermodynamic descriptions either in their energetic or informational aspects. It is a well-known fact that only 0.001% of all mutations can be ascribed to ionizing radiation. The rest of them are caused by thermal fluctuations, and can be described in terms of thermodynamic variables. On the other hand, the process of selection seems to be somehow related to the information content of competing species and individuals. For populations of organisms, the average information level is maximal when there is a free choice of genotype variants available for selection.

The direction of evolution based on random mutations and the process of selection can be formulated in terms of increasing morphological and functional differentiation. As we know, populations of organisms tend to evolve in the direction of higher differentiation, better adaptivity in reproduction, more rapid development and intensive growth. All these signs of increasing informational content in organisms have their corresponding counterparts in energetic terms: I. Schmalgauzen (1968) stressed that indeed there is a correlation between the energy and information metabolism in the evolutionary process. On the other hand, species that are stable with respect to environmental fluctuations have a larger survival potential. Stability of a species corresponds to an organism's low entropy production and a greater selective advantage. Low entropy production is, in turn, associated with a more efficient way to utilize energy.

In other words, progressive evolution tends to select organisms which are most able to utilize energy and to collect information (negentropy) from their environment. Species that occupy higher levels of the

evolutional hierarchy stand higher in the energy pyramid and have a more developed nervous system. In fact, carnivores can obtain their highly energetic food principally because of their developed systems of reflexes. Furthermore, the speed of conditional reflex formation has been shown to be inversely proportional to the entropy of a conditional signal. This corresponds to the notion that in comparative phylogenetic series, there tends to be an increase in the ability to receive redundant information and to forecast events (Zingerman, 1973). Thus, in the process of evolution, the nervous system becomes more organized and the negentropy of living organisms increases. One should always remember, however, that the qualitative aspects of information are often more important for evolution than the actual increase of information influx but that a qualitative information theory has not yet been developed.

To sum up, we may conclude that the concepts of entropy and infromation in the general framework of irreversible thermodynamics may be useful in explaining the directed evolutionary process.

CONCLUDING REMARKS

We have seen how the essential life processes may be expressible in terms of thermodynamic variables. Prigogine's theorem opened new perspectives for the thermodynamics of open systems and,with other developments, make the formalism of irreversible thermodynamics applicable to such phenomena as prebiological evolution.

One should notice, however, that Prigogine's theorem does not distinguish between a living organism and a nonliving <u>open</u> system (such as certain inorganic chemical reactions, etc.). It was suggested by Trincher

(1963) that Prigogine's theorem does not adequately describe such essential life processes as embryogenesis, reproduction and evolution. There are periods during these processes when entropy production actually increases with time. Trincher has argued that the main difference between living and nonliving operating systems (organisms and mechanisms) lies in the fact that all mechanisms lose their structure as a result of their own existence. They also experience an irretrievable loss of information due to noise, thermal fluctuations, etc. On the other hand, in organisms, both structure and information are retained.

Unlike Ashby's homeostat (Ashby, 1952), a living system finds itself in a state of continuous adaptation during which the level of homeostasis undergoes a progressive change in connection with the growing complexity of the organism's functions. The developing brain acquires the ability to react to lesser and lesser deviations of physiochemical parameters from their mean homeostatic values.

These and other competing thermodynamic explanations of biological phenomena show that nonequilibrium thermodynamics is presently in a process of rapid development. It helps to unify diverse biological phenomena, suggests novel experiments and points of view and has a high predictive value. Although a wealth of interesting studies on the problems of biological thermodynamics has been done recently, the field remains open to further investigations.

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APPENDIX

Exact Differentials

Given a function $z = f(x,y)$ defined in some neighborhood of the piont (x_0,y_0), and the increments of independent variables dx and dy, the differential of z at the point (x_0,y_0) is expressed as

$$dz = \left.\frac{\partial f}{\partial x}\right|_{x_0,y_0} dx + \left.\frac{\partial f}{\partial y}\right|_{x_0,y_0} dy \quad . \tag{47}$$

The differential is exact if

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \quad . \tag{48}$$

When (48) does not hold, z cannot be uniquely defined by x and y and, in this case, we say that dz is not an exact differential of variables x and y. It should be noted here that the differentials of thermodynamic functions of state are always exact. However, when we represent dS as the sum of d_iS and d_eS, they may not, in general, be exact differentials of the independent variables (say, time and temperature).

ANSWERS TO SELECTED EXERCISES

pp. 20-21

1. Take all the elements that constitute a living cell and combine them randomly. The resulting subtotal of elements is not equal to the system. An important feature of the systems, namely interaction of elements, is stressed by this example.
2. Death.
5. This is an example of the hierarchy of the system's elements. The system is open.
6. Closed, because no matter is practically exchanged between the earth and outer space.

pp. 23-24

1. If we write the energy balance as

$$Q_{abs} = Q_{rad} + Q_{cond} + Q_{conv} + Q_{evap}$$

(where Q's in the order listed stand for the rate of energy transfer of absorption, radiation, conduction, convection and evaporation, respectively), then an increase, say, in temperature, may lead to the corresponding increase in Q_{evap} and, as a consequence, in Q_{abs}.

2. $dU = dQ - dW$ where dU is the total amount of energy gained or lost by an animal in time, dt,

dQ = heat production

dW = physiological work needed for activity .

pp. 29-30

1. (1) -24.25 e.u.; (2) -24.25 e.u.; (3) 0; (4) 0.

p. 49

1. 1; 0.

pp. 59-60

1. In closed systems, negentropy decreases with time.
2. State II.
3. About 3×10^{20} pages.

APPENDIX: Symbols, Units and Dimensions

Symbol	Definition	Unit	Dimension
A	Area	m^2	L^2
A	Chemical affinity	J	ML^2T^{-2}
a	Constant	s^{-1}	T^{-1}
a	Chemical component	---	---
B	Area of boundary	m^2	L^2
c_p	Specific heat at constant pressure	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
c_v	Specific heat at constant volume	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
C	Concentration	$kg\ m^{-3}$	ML^{-3}
E	Excreted matter	kg	M
F	Force	N	MLT^{-2}
F	Thermodynamic force	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
G	Gibbs free energy	J	ML^2T^{-2}
H	Enthalpy	J	ML^2T^{-2}
H_c	Enthalpy of consumer	J	ML^2T^{-2}
H_p	Enthalpy of producer	J	ML^2T^{-2}
H_m	Net change enthalpy	J	ML^2T^{-2}

APPENDIX (cont.)

Symbol	Definition	Unit	Dimension
I	Enthalpy content of ingested matter	J	ML^2T^{-2}
I	Information	bit	---
I_{ave}	Average information	bit	---
K'	Constant	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
K	Constant	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
K	Boltzmann constant	1.38×10^{-13} $J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
L	Constant (phenomenological coefficient)	$K^{-1}J^{-1}$	$M^{-1}L^{-2}T\theta$
L	Displacement	m	L
M	Molecular weight	kg	M
m	Mass	kg	M
N	Negentropy	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
n	Change in mass	---	---
n	Number of moles	---	---
P	Entropy production	$J\ K^{-1}\ s^{-1}$	$ML^2T^{-3}\theta^{-1}$
P_i	Number of choices before obtaining information I	---	---

APPENDIX (cont.)

Symbol	Definition	Unit	Dimension
P_2	Number of choices after obtaining information I	---	---
$d_A P$	Differential entropy production due to flows	$J\ K^{-1}\ s^{-1}$	$ML^2T^{-3}\theta^{-1}$
$d_F P$	Differential production due to thermodynamic forces	$J\ K^{-1}\ s^{-1}$	$ML^2T^{-3}\theta^{-1}$
P	Mathematical probability of a given macroscopic state	---	---
p	Pressure	$N\ m^2$	$ML^{-1}T^{-2}$
Q	Heat	J	ML^2T^{-2}
Q_o	Initial number of organisms	---	---
Q	Number of organisms	---	---
q	Heat flux	$J\ s^{-1}$	ML^2T^{-3}
R	Heat loss due to respiration	J	ML^2T^{-2}
R	Universal gas constant	8.3×10^{13} $J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
S	Entropy	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
$d_e S$	External entropy (differential increment)	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$
$d_i S$	Internal entropy (differential increment)	$J\ K^{-1}$	$ML^2T^{-2}\theta^{-1}$

APPENDIX (cont.)

Symbol	Definition	Unit	Dimension
t	Time	s	T
U	Internal energy	J	ML^2T^{-2}
V	Volume	m^3	L^3
v	Velocity of reaction	kg s^{-1}	MT^{-1}
W	Work	J	ML^2T^{-2}
W	Thermodynamic probability of a given state	---	---
W_o	Total number of completions possible	---	---
y	Extent of reaction	---	---
Φ	Dissipation function	J K^{-1} s^{-1}	$ML^2T^{-3}\theta^{-1}$
ν	Stoichiometric coefficient	---	---
θ	Temperature	K	θ
θ_o	Temperature of the animal	K	θ
θ_e	Temperature of the environment	K	θ
μ	Chemical potential	J	ML^2T^{-2}